# Synthesis and Spectroscopic Properties of some New Seven-coordinate Thioacetamide Complexes of Molybdenum(II) and Tungsten(II)

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## Abstract

The compounds $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with one equivalent of $SC(NH_2)Me$ in $CH_2Cl_2$ at room temperature to initially give the acetonitrile substituted products $[MI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$ which was isolated for M = W. However, the molybdenum complex rapidly dimerizes with loss of acetonitrile to give the iodide-bridged compound $[Mo(\mu\text{-}I)I(CO)_3\{SC(NH_2)Me\}]_2$. The tungsten complex does not appear to dimerize, even after stirring at room temperature for 72 h in $CH_2Cl_2$. Two equivalents of thioacetamide react with $[MI_2(CO)_3(NCMe)_2]$ in $CH_2Cl_2$ at room temperature to give the new bisthioacetamide compounds $[MI_2(CO)_3\{SC(NH_2)Me\}_2]$ via displacement of the labile acetonitrile ligands. The low temperature (−70 °C) $^{13}C$ NMR spectrum of $[WI_2(CO)_3\{SC(NH_2)Me\}_2]$ indicates that the geometry of the complex is capped octahedral with a carbonyl ligand in the unique capping position.

## Introduction

Seven-coordinate complexes have become increasingly important in recent years; in particular the compounds $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl or Br; L = $PPh_3$ or $AsPh_3$) which have recently been found to be catalysts for the ring-opening polymerization of norbornene and norbornadiene [1, 2]. Although a wide variety of complexes of the type $[M(CO)_n(S_2CNR_2)_2]$ (M = Mo or W; $n$ = 2 or 3; R = Me, Et or $^iPr$) containing anionic sulphur donor ligands have been extensively investigated [3–8] very few seven-coordinate complexes containing neutral sulphur donor ligands have been reported.

In this paper we wish to describe the preparation and properties of some new thioacetamide seven-coordinate compounds of molybdenum(II) and tungsten(II).

## Experimental

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were prepared according to the literature method [9]. All chemicals used were purchased from commercial sources. Dichloromethane was distilled before use. $^1H$ NMR spectra were recorded on a Jeol FX60 NMR spectrometer. The low temperature (−70 °C) $^{13}C$ NMR spectrum of $[WI_2(CO)_3\{SC(NH_2)Me\}_2]$ was recorded on a Bruker WH-400 NMR spectrometer at the University of Warwick. All NMR spectra were calibrated against tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer.

Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium carrier gas). The molecular weights were determined by Rast's method [10] using camphor as the solvent. Magnetic susceptibilities were measured using a Johnson-Matthey magnetic susceptibility balance.

### $[Mo(\mu\text{-}I)I(CO)_3\{SC(NH_2)Me\}]_2$ (1)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.206 g, 0.399 mmol) dissolved in $CH_2Cl_2$ (15 $cm^3$) with continuous stirring under a stream of dry nitrogen was added $SC(NH_2)Me$ (0.03 g, 0.399 mmol). After stirring the solution for 1 min, filtration, removal of solvent *in vacuo* gave brown crystals of $[Mo(\mu\text{-}I)I(CO)_3\{SC(NH_2)Me\}]_2$ (yield = 0.12 g, 59%), which were recrystallized from $CH_2Cl_2$. *Anal.* Calc. for $C_{10}H_{10}N_2O_6I_4Mo_2S_2$: C, 11.8; H, 1.0; N, 2.8. Found: C, 12.3; H, 1.4; N, 2.8%. Magnetic susceptibility of **1** is $-0.217 \times 10^{-6}$ c.g.s. Molecular weight for **1**, $C_{10}H_{10}N_2O_6I_4Mo_2S_2$: calc. 1018; found, 862.

### $[WI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$ (2)

To $[WI_2(CO)_3(NCMe)_2]$ (0.233 g, 0.386 mmol) dissolved in $CH_2Cl_2$ (15 $cm^3$) with continuous stirring under a stream of dry nitrogen was added $SC(NH_2)Me$ (0.029 g, 0.386 mmol). After stirring the solution for 30 s, filtration, removal of solvent *in vacuo* gave yellow crystals of $[WI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$ (yield = 0.20 g, 81%), which were

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recrystallized from $CH_2Cl_2$. *Anal.* Calc. for $C_7H_8N_2O_3I_2WS$: C, 13.2; H, 1.3; N, 4.4. Found: C, 13.6; H, 1.4; N, 4.1%. Magnetic susceptibility of 2 is $-0.432 \times 10^{-6}$ c.g.s. Molecular weight for 2, $C_7H_8N_2O_3I_2WS$: calc. 638; found, 571.

### $[MoI_2(CO)_3\{SC(NH_2)Me\}_2]$ (3)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.206 g, 0.399 mmol) dissolved in $CH_2Cl_2$ (15 $cm^3$) with continuous stirring under a stream of dry nitrogen was added $SC(NH_2)Me$ (0.06 g, 0.799 mmol). After stirring the solution for 6 min, filtration, removal of solvent *in vacuo* gave orange crystals of $[MoI_2(CO)_3\{SC(NH_2)Me\}_2]$ (yield = 0.14g, 60%), which were recrystallized from $CH_2Cl_2$. *Anal.* Calc. for $C_7H_{10}N_2O_3I_2MoS_2$: C, 14.4; H, 1.7; N, 4.8. Found: C, 14.2; H, 1.7; N, 4.4%.

### $[WI_2(CO)_3\{SC(NH_2)Me\}_2]$ (4)

To $[WI_2(CO)_3(NCMe)_2]$ (0.233 g, 0.386 mmol) dissolved in $CH_2Cl_2$ (15 $cm^3$) with continuous stirring under a stream of dry nitrogen was added $SC(NH_2)Me$ (0.058 g, 0.772 mmol). After stirring the solution for 8 min, filtration, removal of solvent *in vacuo* gave orange crystals of $[WI_2(CO)_3\{SC(NH_2)Me\}_2]$ (yield = 0.16 g, 62%), which were recrystallized from $CH_2Cl_2$. *Anal.* Calc. for $C_7H_{10}N_2O_3I_2S_2W$: C, 12.5; H, 1.5; N, 4.2. Found: C, 12.5; H, 1.5; N, 3.8%.

## Results and Discussion

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $SC(NH_2)Me$ react in $CH_2Cl_2$ at room temperature to afford the new dinuclear molybdenum complex $[Mo(\mu\text{-}I)I(CO)_3\{SC(NH_2)Me\}]_2$ or the mononuclear tungsten compound $[WI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$. $[MI_2(CO)_3(NCMe)_2]$ reacts with two equivalents of $SC(NH_2)Me$ in $CH_2Cl_2$ at room temperature to give the new seven-coordinate compounds $[MI_2(CO)_3\{SC(NH_2)Me\}_2]$. All the complexes have been fully characterized by elemental analysis (C, H and N) (see 'Experimental'), IR and $^1H$ NMR spectroscopy (Table I). The complexes are moderately stable in the solid state when stored under nitrogen at 0 °C, but decompose rapidly in solution when exposed to air. They are moderately soluble in $CHCl_3$ and $CH_2Cl_2$ and very much more soluble in MeOH.

Reaction of one equivalent of $SC(NH_2)Me$ with $[MoI_2(CO)_3(NCMe)_2]$ at room temperature in $CH_2Cl_2$ must initially afford the monoacetonitrile compound $[MoI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$. This rapidly dimerizes with loss of the weakly bound acetonitrile ligand to give the iodide-bridged product $[Mo(\mu\text{-}I)I(CO)_3\{SC(NH_2)Me\}]_2$ which was isolated. Whereas reaction of one equivalent of $SC(NH_2)Me$ with $[WI_2(CO)_3(NCMe)_2]$ gives the monoacetonitrile product $[WI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$, surprisingly, stirring $[WI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$ in $CH_2Cl_2$ at room temperature for 72 h did not afford the dimeric complex $[W(\mu\text{-}I)I(CO)_3\{SC(NH_2)Me\}]_2$. The monoacetonitrile monomer (2) and some decomposition products were isolated. A possible explanation for this behaviour is due to the slightly smaller size of the Mo(II) ion compared to the W(II) ion. Hence $[MoI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$ loses NCMe to release steric strain around the molybdenum centre to give the six-coordinate intermediate $[MoI_2(CO)_3\{SC(NH_2)Me\}]$ which then rapidly dimerizes via attack of the iodide lone pairs. Evidence to support this dissociative mechanism comes from some work reported by Tripathi and co-workers [11]. They reacted $[Mo(CO)_5L]$ (L = $PPh_3$, $AsPh_3$ or $SbPh_3$) with $X_2$ (X = Cl, Br or I) in hexane which resulted in the immediate precipitation of the coordinatively unsaturated '16-electron' compounds $[MoX_2(CO)_3L]$. The dimeric nature of the seven-coordinate

TABLE I. Infrared[a] and $^1H$ NMR[b] Data for the Complexes $[Mo(\mu\text{-}I)I(CO)_3\{SC(NH_2)Me\}]_2$, $[WI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$ and $[MI_2(CO)_3\{SC(NH_2)Me\}_2]$

| Complex | $\nu$(CO) ($cm^{-1}$) | $\nu$(CN) ($cm^{-1}$) | $\nu$(CS) ($cm^{-1}$) | $^1H$ NMR ($\delta$) (ppm)[b] | | |
|---|---|---|---|---|---|---|
| | | | | NCMe | Me | $NH_2$ |
| 1 $[Mo(\mu\text{-}I)I(CO)_3\{SC(NH_2)Me\}]_2$ | 2075(m), 2035(s), 1960(m) | | 1619(s) | | | [c] |
| 2 $[WI_2(CO)_3(NCMe)\{SC(NH_2)Me\}]$ | 2080(s), 2035(s), 1942(brs) | 2320(w), 2298(w) | 1617(s) | 1.99(s, 3H) | 2.77(s, 3H) | [c] |
| 3 $[MoI_2(CO)_3\{SC(NH_2)Me\}_2]$ | 2020(s), 1958(s), 1930(s) | | 1613(s) | | 2.65(s, 3H) | 3.60(s, 2H) |
| 4 $[WI_2(CO)_3\{SC(NH_2)Me\}_2]$ | 2020(s), 1943(s), 1920(s) | | 1613(s) | | 2.70(s, 3H) | 3.34(s, 2H) |

[a] Spectra recorded in $CHCl_3$ or MeOH; s, strong; m, medium; w, weak. [b] Spectra recorded in $CDCl_3$ (+25 °C) referenced to $Me_4Si$. [c] No $NH_2$ resonance was observed for these complexes.

complex $[Mo(\mu\text{-}I)I(CO)_3\{SC(NH_2)Me\}]_2$ is confirmed by magnetic susceptibility and molecular weight measurements (see 'Experimental').

Reaction of $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of $SC(NH_2)Me$ at room temperature in $CH_2Cl_2$ rapidly gave the expected $[MI_2(CO)_3\{SC(NH_2)Me\}_2]$ compounds. In view of the similarity of the carbonyl IR pattern to other analogous seven-coordinate compounds which have been shown to have capped octahedral geometry from X-ray crystallography [12–20], it is highly likely that **3** and **4** have capped octahedral geometry. This is further supported by the low temperature (–70 °C) $^{13}C$ NMR spectrum ($CD_3OD$) of $[WI_2(CO)_3\{SC(NH_2)Me\}_2]$ which shows two carbonyl resonances at $\delta = 206.40$ and 231.96 ppm. Colton and Kevecordes [21] have shown how low temperature $^{13}C$ NMR spectroscopy can be used to see if there is a carbonyl ligand in the unique capping position by the presence of a low field carbonyl resonance. Hence the low field resonance at $\delta = 231.96$ ppm for **4** is probably due to a carbonyl ligand in the unique capping position, and the resonance at $\delta = 206.40$ is due to two equivalent carbonyls in normal octahedral environments. Many attempts were made to grow crystals of $[MI_2(CO)_3\text{-}\{SC(NH_2)Me\}_2]$ suitable for X-ray crystallography without success.

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